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DYNAMICS AND RHEOLOGY OF LINEAR ENTANGLED POLYMER NANOCOMPOSITES

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EXTENDED ABSTRACT

Polymers filled with nanoparticles have attracted considerable technological and scientific interest during the recent past, because of dramatic enhancements in physical, thermal, and mechanical properties observed experimentally. It is necessary to understand the rheological behavior of such mixtures so as to improve their manufacturing procedure.

The structure and dynamics of confined and near-surface entangled polymers is strongly affected by the entanglements between polymer chains and the polymer-particle surface affinity.

The most successful theory that takes into account the effect of entanglements is based on the tube model (Doi and Edwards 1986; Mead et al. 1998; Marrucci and Ianniruberto 2003). The physical picture underlying the tube model of polymer dynamics is that the motion of any chosen polymer chain is strongly restricted by the presence of surrounding polymers, which create a sort of a tube around the chosen chain. Such chains can interact strongly due to the topological constraints that chains cannot cross each other.

In polymer systems filled with nanoparticles, molecular dynamics simulations (Picu and Rakshit 2007) showed that, the slowing down of polymer chain dynamics is due to the energetic polymer-particle interaction. The effect varies monotonically with the polymer-particle affinity. Recent molecular dynamics simulations (Subbotin et al. 1997) suggested that the polymer-surface interactions can be the dominant factor in the rheology of confined systems. These interactions include the short-range forces between the surfaces and the polymer segments. These forces can be responsible for the suppression of the mobility of the polymer segments at the surfaces and even result in the formation of an immobilized glassy layer at the surfaces. Dionne et al. (2005) studied the structure and dynamics of an amorphous polyethylene (PE) melt containing homogeneously distributed spherical nanoparticles. The PE chains were simulated using both molecular dynamics and Monte Carlo methods. The chain dynamics were monitored by computing the Rouse relaxation modes and the mean-square displacement (MSD). The most notable observation they pointed out, was the slowing down in the Rouse dynamics seen on all subsections of the chain no matter how small the subsections were, meaning that on average every monomer feels the confinement of the neighboring particles, slowing the relaxation of every chain subsection. They also showed that the slowing down due to polymer-particle energetic interaction was similar for all relaxation modes, independent of their wavelength. Shaffer (1996) investigated the effects of chain topology on the dynamics of confined polymer melts by conducting computer simulations. Their results suggest that entanglements are neither induced nor enhanced by confinement between impenetrable adsorbing surfaces. Taking advantage of these insights, we apply the tube-based model (the reptation theory) with an effective relaxation time to treat the dynamics of chain entanglements in the presence of attractive impenetrable nanoparticles.

In this paper, a reptation-based model, that incorporates transient polymer-particle surface interactions, is proposed to describe the dynamics and rheological behaviors of linear entangled polymers filled with isotropic rigid nanoscale particles. Dispersed nanoparticles are sufficiently small such that even at low volume fractions, the average particle wall-to-wall distance is on the order of the chain size. Using the theory of the activation process, it is shown that the polymer-particle interactions give rise to an exponential increase of the characteristic time, τ_g, for the detachment of all trapped monomers in the chain, from nanoparticle surfaces, i.e,

$\tau_g \propto \exp\left[\varepsilon\theta_a \frac{\phi_f n_{as}}{d_f} N^{3/2} b^3\right]$, where N is the number of monomers per polymer chain, b the length of a monomer, d_f the diameter of nanoparticles, ε a parameter representing the polymer-particle energetic interaction, θ_a the fraction of attractive sites on the nanoparticle surface occupied by monomers, n_{as} the number of attractive sites per unit surface of the nanoparticle, and ϕ_f the nanoparticle volume fraction. Hence, the effective reptation time for the overall motion of the chain turns out to be exponentially large with the nanoparticle addition, leading to a slowing down of the reptation dynamics. The nonequilibrium dynamics of detachment/re-attachment of monomers from/to nanoparticle surfaces under flow conditions is incorporated in the model to elucidate the effects of monomer-surface interactions on the nonlinear viscoelastic behavior. The resulting model correctly captures the linear dynamical properties and shear rheological behaviors of nanocomposite systems studied (Figs. 1-4). Under very slow shear flow conditions, these filled systems exhibit a strong non-Newtonian behavior and a large enhancement in the viscosity as a certain number of monomers in the chain are attached to nanoparticle surfaces, while at very high shear rates, the neat polymer dominates the shear thinning behavior, suggesting that addition of nanoparticles contributes negligible to the viscosity in strong flows. A picture that is based on transient polymer-particle surface interactions, i.e., the detachment/re-attachment dynamics of monomers from/to nanoparticle surfaces is proposed to interpret the observed huge alteration in rheological properties.

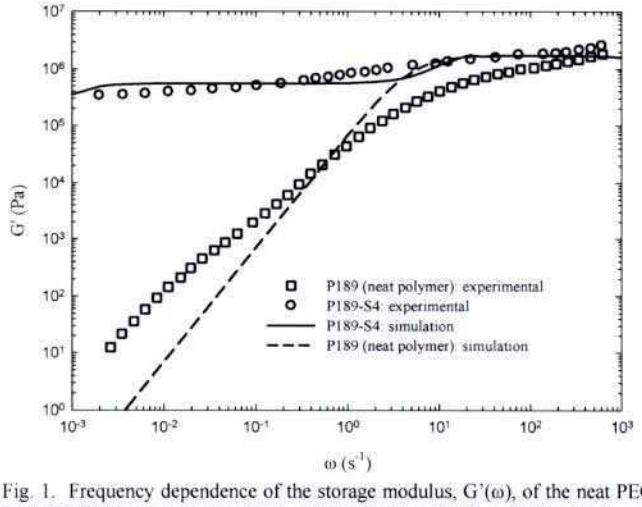

Fig. 1. Frequency dependence of the storage modulus, G'(ω), of the neat PEO and a PEO/silica nanocomposite at volume fraction of 4 %, with fixed polymer-particle energetic interaction parameter, ε = 1.5. Experimental results are from Zhang and Archer (2002).

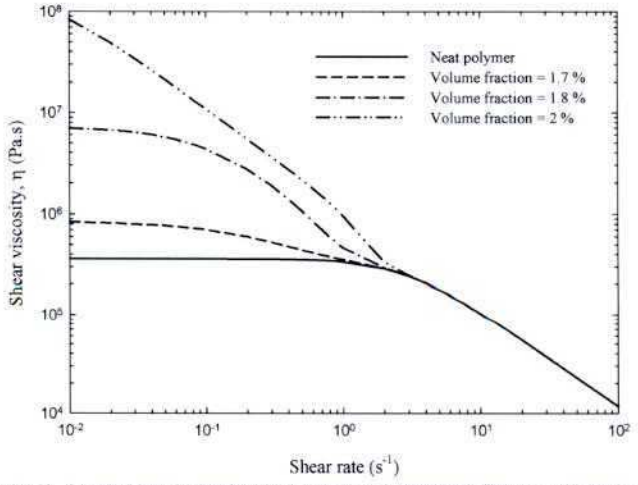

Fig. 2. Steady shear viscosity of PEO/silica nanocomposites as a function of shear rate with fixed polymer-particle energetic interaction parameter, ε = 1.7, and different volume fractions.

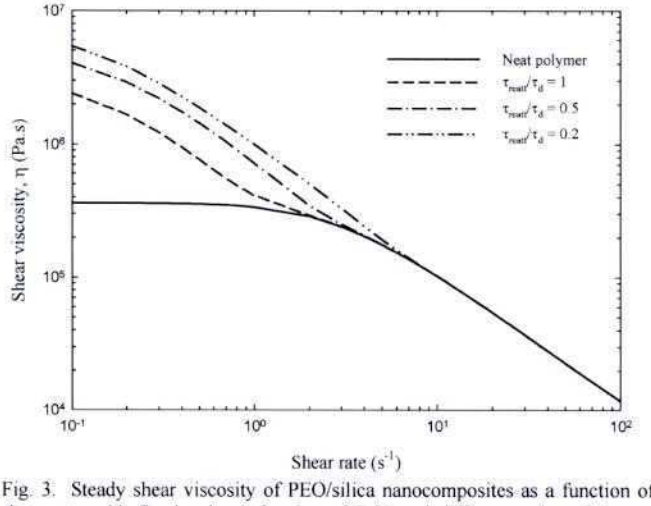

Fig. 3. Steady shear viscosity of PEO/silica nanocomposites as a function of shear rate with fixed volume fraction of 2 % and different ratios of the re-attachment time, τ_{reatt}, and reptation time, τ_d.

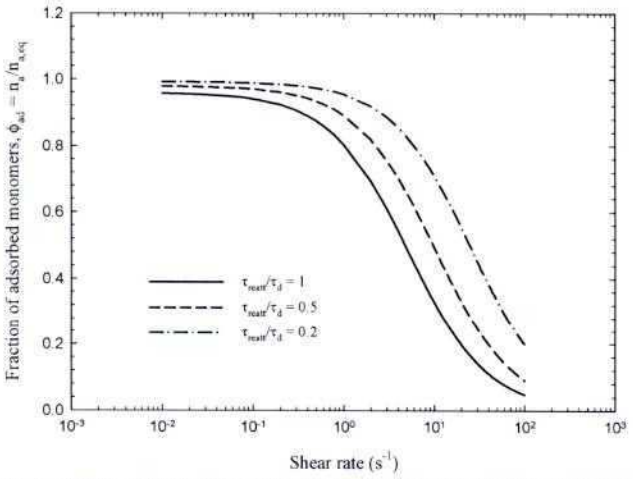

Fig. 4. Steady-state fraction of adsorbed monomers as a function of shear rate with fixed volume fraction of 2 % and different ratios of the re-attachment time, τ_{reatt}, and reptation time, τ_d.

REFERENCES

Dionne, P.J., C.R. Picu, and R. Ozisik, "Adsorption and desorption dynamics of linear polymer chains to spherical nanocomposites: A monte Carlo investigation," Macomolecules. **39**, 3089-3092 (2006).

Doi, M., and S.F. Edwards, "The theory of polymer dynamics," Clarendon: New York (1986).

Marrucci, G., and G. Iannirubertо "Flow-induced orientation and stretching of entangled polymers," Phil. Trans. R. Soc. Lond. A **361**, 677-688 (2003).

Mead, D.W., R.G. Larson, and M. Doi, "A molecular theory for fast flows of entangled polymers," Macromolecules **31**, 7895-7914, (1998).

Picu, R.C., and A. Rakshit, "Dynamics of free chains in polymer nanocomposites," The J. Ch. Phys. **126**, 144909-1 (2007).

Shaffer, J.S., "Dynamics of confined polymer melts: Topology and Entanglement," Macromolecules **29**, 1010-1013 (1996).

Subbotin, A., A. Semenov, and M. Doi, "Friction in strongly confined polymer: effect of polymer brodges," Phys. Rev. E. **56**, 623-630 (1997).

Zhang, Q., and L.A. Archer, "Poly(ethylene oxide)/Silica nanocomposites: Structure and rheology," Langmuir. **18**, 10435-10442 (2002).